

RESEARCH ARTICLE

View Article Online
View Journal | View Issue

Cite this: *Mater. Chem. Front.*,
2025, 9, 3460

Received 26th April 2025,
Accepted 13th October 2025

DOI: 10.1039/d5qm00333d

rsc.li/frontiers-materials

Organic afterglow coating materials via emulsion polymerization

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Organic room-temperature phosphorescent (RTP) materials are of increasing interest due to their unique triplet-state emission and potential applications in anti-counterfeiting, bioimaging, and optical storage. However, challenges such as low emission efficiency, short lifetimes, and limited scalability have hindered their practical use. Herein, we report a facile and scalable synthesis of difluoroboron β -diketonate (BF_2bdk) compounds and their incorporation into a poly(methyl methacrylate) (PMMA) matrix via emulsion polymerization. The rigid microenvironment of PMMA effectively suppresses non-radiative decay of the triplet state, yielding an RTP emulsion with a phosphorescence lifetime of up to 1.38 s. Blending with commercial emulsions enables the fabrication of uniform, transparent RTP coatings that can be obtained with bright afterglow exceeding 10 s. These coatings exhibit excellent environmental stability, thermal and chemical resistance, and industrial applicability. This study addresses the long-standing challenge of the scalable fabrication of aqueous afterglow materials, and offers a promising route for the large-scale production of high-performance organic RTP materials, paving the way for their integration into diverse application scenarios such as advanced optical and security technologies.

Introduction

Room-temperature phosphorescence and organic long persistent luminescence materials have attracted significant attention due to their intriguing luminescent properties. Materials with afterglow characteristics show broad application prospects in fields such as secure inks, biomedicine, anti-counterfeiting, displays, and lighting, as well as environmental monitoring.^{1–21} The long lifetime of organic RTP materials originates from the triplet excited state of the luminescent molecules. To obtain long-lived afterglow materials, it is necessary to suppress non-radiative deactivation and oxygen quenching of the luminescent molecules. To achieve high phosphorescence yield and long-lifetime RTP materials, strategies such as molecular design and supramolecular self-assembly have been developed.^{22–31} For example, the introduction of halogen atoms or other heavy atoms into organic systems can promote intersystem crossing (ISC) and enhance the phosphorescence quantum yield,¹⁰ though this may simultaneously reduce the phosphorescence lifetime. Supramolecular macrocycles can

form stable host–guest complexes with luminescent molecules via supramolecular interactions such as hydrogen bonding and the hydrophobic effect. The cavity of the supramolecular host molecule provides a rigid microenvironment for the guest molecules, suppressing non-radiative deactivation caused by molecular vibrations, thus enabling the development of RTP materials.^{32–36} However, large-scale application and production of organic room-temperature afterglow materials are still rarely reported.

Water-based polymer coatings play a crucial role in the coating industry due to their ease of use and excellent physical properties. They have been widely applied in various fields such as construction and the automotive industry. Polymer coatings can form a continuous, dense layer on the surface of objects, effectively isolating external corrosive substances while maintaining high transparency. However, reports on the large-scale preparation of organic water-based polymer afterglow coatings are still scarce.^{9,15,32–36}

In recent years, the two-component strategy has become an efficient approach for manufacturing organic room-temperature phosphorescent materials.^{2,6,10,19–21} By introducing a second component, the excited-state properties of the luminescent molecules can be tuned, suppressing non-radiative deactivation of the triplet excited state and oxygen quenching, while simultaneously promoting the intersystem crossing process in organic systems.^{15,18,37–45} According to the formula $\tau_p = 1/(k_p + k_{nr} + k_q)$,^{46–52} it is clear that reducing non-

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radiative decay and oxygen quenching ($k_{nr} + k_q$) can extend the phosphorescence lifetime (τ_p), which can be achieved by selecting an organic matrix or polymer matrix that provides a rigid microenvironment for the luminescent molecules. Both our work and that of others have reported that the two-component strategy can achieve long-lifetime phosphorescent emission. For example, using carbonyl-containing organic molecules such as phenyl benzoate (PhB) as the second component can generate dipole-dipole interactions with the luminescent molecules,^{43,44} resulting in high quantum yield and long-lifetime RTP materials. However, most of these long-lifetime afterglow materials are prepared using melt-casting and mechanical grinding methods, producing bulk or powdered solids.^{1,30,45–63} Although using the molten droplet method, along with ultrasonic treatment and surfactants to disperse the afterglow materials in an aqueous solution, stable water-based afterglow dispersions can be obtained, and the inherent rigid microenvironment is destroyed, leading to a significant reduction in phosphorescence lifetime.^{63,64} In contrast, when the luminescent molecules are encapsulated in polymer latex in an emulsion system, the non-radiative deactivation of the luminescent molecules is significantly suppressed by the polymer latex.^{61,64} The obtained water-based afterglow emulsions, prepared under degassed conditions, exhibit phosphorescence lifetimes on the order of seconds. The emulsion polymerization system, where luminescent molecules are doped into monomers, lays the foundation for large-scale preparation of water-based afterglow emulsions (Scheme 1).

Results and discussion

In this study, we used inexpensive industrial-grade fluorene as the raw material and synthesized 4-(9H-fluoren-2-yl)-2,2-

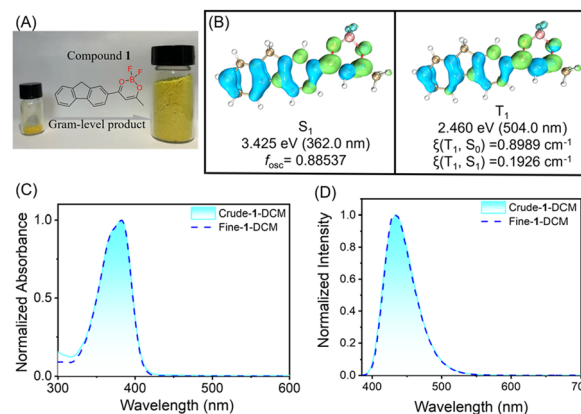
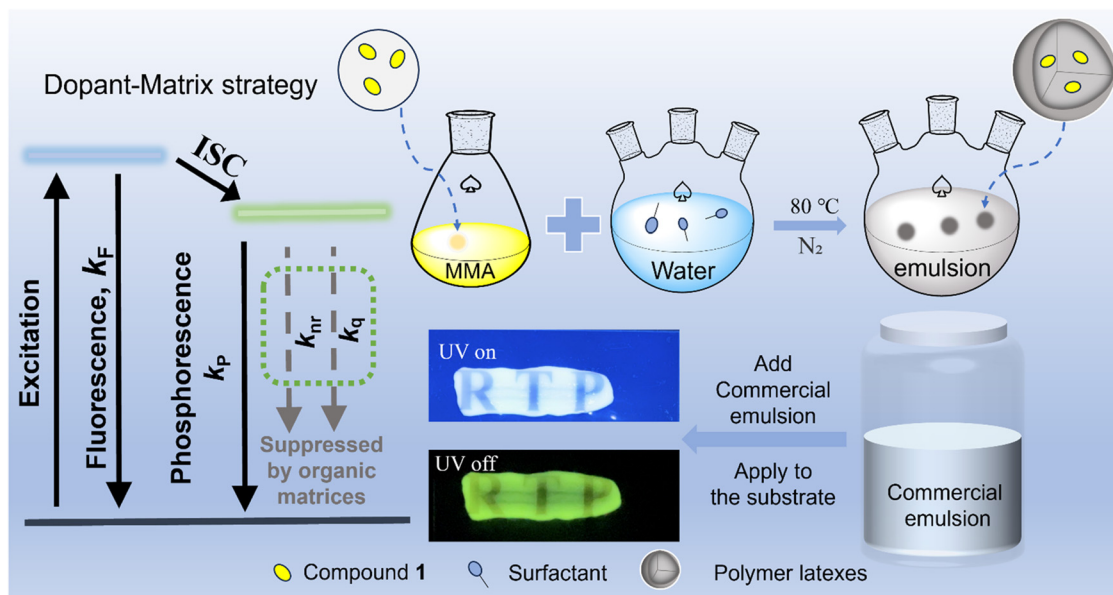


Fig. 1 (A) Photograph and chemical structure of compound **1**. (B) TD-DFT calculation results of **1** at the level of B3LYP/6-31G (d, p). (C) UV-vis spectra of crude-**1** and fine-**1** in dichloromethane. (D) Room-temperature steady-state emission spectra of crude-**1** and fine-**1** in dichloromethane.

difluoro-6-methyl-2H-1,3 λ^3 ,2 λ^4 -dioxaborinine (compound **1**, Fig. 1A and Fig. S1) through a cascade reaction previously reported.⁶⁵ After filtering the reaction solution with silica gel powder, the filtrate was treated with ice-cold ether to precipitate the product. Detailed information about the synthesis process, structure, and purity of compound **1** can be found in the Supplementary Information. The crude product of compound **1** and the purified compound **1** exhibit identical photophysical properties. Both show the same solution fluorescence ranging from 400 nm to 500 nm in dichloromethane (photoluminescence quantum yields of 93%), with identical fluorescence maxima at 433 nm and band shapes. The UV-vis absorption in solution also displays the same absorption bands and similar molar absorption coefficients around $3.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ (Fig. 1B–D). The structure of compound **1** was confirmed by



Scheme 1 Proposed mechanism of room-temperature phosphorescence in the dopant-matrix strategy and flow diagram of a large-scale synthetic phosphorescent emulsion and its application on a patterned substrate.



^1H NMR, ^{11}B NMR, ^{13}C NMR, ^{19}F NMR, and ESI-MS. Their high purity was further confirmed by HPLC measurement.

Comparing the photophysical properties of two-component samples with different purities is crucial for excluding the influence of impurity-related luminescence mechanisms in this study. To investigate the impact of impurity-induced luminescence mechanisms, we employed a two-component strategy, doping compound **1** with different purities into phenyl benzoate (PhB) and 4-methoxybenzophenone (MeOBP). Both the crude compound **1** and the purified compound **1** in the organic matrices exhibited identical photophysical properties. Both crude **1**-PhB-0.01% and purified **1**-PhB-0.01% displayed the same bright blue fluorescence and green afterglow. This is because the organic matrix with carbonyl functional groups can promote intersystem crossing through dipole-dipole interactions, leading to efficient organic afterglow. The photophysical data also showed identical fluorescence and phosphorescence maxima, as well as similar band shapes and phosphorescence lifetimes (Fig. 2). When the organic matrix was changed to MeOBP, the conclusions remained the same (Fig. S2). This excludes the influence of impurity-induced afterglow mechanisms on our system (Fig. S3), confirming that the presence of impurities is not the cause of the afterglow and does not interfere with phosphorescent emission. This finding simplifies the complex synthesis processes of luminescent molecules and further reduces the cost of preparing these molecules, laying the foundation for the large-scale preparation of afterglow emulsions.

Based on this, compound **1** was dissolved into methyl methacrylate (MMA) monomers for emulsion polymerization, resulting in an emulsion with bright green afterglow under degassed conditions. The rigid microenvironment of PMMA suppresses the non-radiative deactivation of compound **1**'s triplet excited state, allowing the afterglow duration of the emulsion to reach up to 10 s (Fig. 3A), with a phosphorescence lifetime of 1.38 s (Fig. 3B and C). The steady-state emission spectrum exhibits a fluorescence band in the range of 385–500 nm, with a maximum emission wavelength at 419 nm (S_1 energy level, 2.96 eV). The delayed emission spectrum (1 ms delay) shows a phosphorescent

band in the range of 500–650 nm, with the maximum emission peak at 523 nm (T_1 energy level, 2.37 eV). Compared with previously reported afterglow emulsions, this study significantly increased the production volume of the afterglow emulsion from a few milliliters to several hundred milliliters in a single preparation (Scheme 1). This allows for the large-scale production of uniform and stable afterglow emulsions, with an average particle size of 206.2 nm (Fig. S4 and S5).

To investigate the photophysical mechanisms of compound **1** in the emulsion system and exclude several potential mechanisms for organic phosphorescence, we conducted a series of experiments. Firstly, the photophysical properties of compound **1** with different purities in PhB and MeOBP indicate that impurities do not affect the photophysical properties (Fig. 1 and Fig. S3). The HPLC analysis of purified compound **1** also confirmed the exclusion of the impurity-induced afterglow mechanism (Fig. S3). Secondly, energy transfer only occurs when the donor is sufficiently excited. The afterglow emulsion in this study can be excited by UV light at 365 nm, but PMMA has negligible absorption at this wavelength, and no afterglow was observed after exciting PMMA only (Fig. S6). This rules out the possibility of room-temperature phosphorescence caused by energy transfer from the PMMA matrix to compound **1**. Thirdly, PMMA has a lower-lying highest occupied molecular orbital (HOMO) and a higher-lying lowest unoccupied molecular orbital (LUMO) compared to compound **1**,⁶⁶ which means that intermolecular charge transfer between compound **1** and the PMMA matrix can be neglected. This eliminates the possibility of an organic long persistent luminescence mechanism in this system. Fourth, the T_1 level of PMMA is higher than both the S_1 and T_1 levels of compound **1**, indicating that there is no T_1 -mediated RTP mechanism in the **1**-PMMA emulsion system. Finally, delayed emission spectra at 77 K ruled out the possibility of a thermally activated delayed fluorescence (TADF) afterglow mechanism (Fig. S7). These results collectively confirm that the afterglow in this system is not due to these alternative mechanisms, thus providing a clearer understanding of the photophysical processes at play.

Compared to the reported methods of nanoprecipitation and supramolecular assembly,^{9,15,32–36} the emulsion polymerization-based method for afterglow material fabrication allows large-scale preparation of aqueous afterglow materials with relatively high solid contents. The key innovation here is the use of as-formed polymer latex to protect the organic triplets, which can eliminate the side effects regarding the disruption of the rigid microenvironment in conventional methods. In the literature, other scalable RTP systems are mainly focusing on powders and films that show excellent quantum yield, lifetime, processability, and cost-effectiveness,^{2,16,22,29} which are different from the present study focusing on aqueous afterglow materials.

To further improve the physical properties of the coating while making the afterglow emulsion commercially viable, four commercially available polymer emulsions were mixed in equal volumes with our prepared afterglow emulsion to obtain binary blend organic afterglow coatings. Coatings A, B, C, and D represent mixtures of afterglow emulsion with silane-acrylic emulsion, butyl acrylate emulsion, acrylic JS high-elasticity

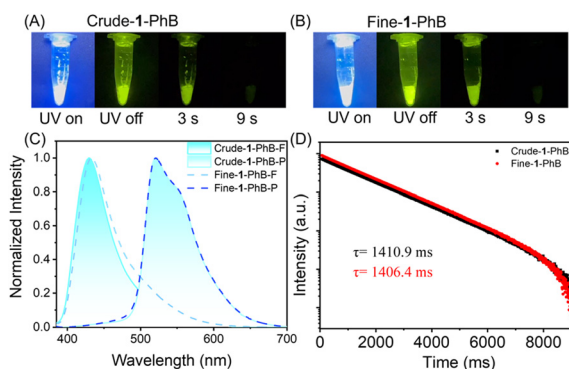


Fig. 2 Photographs of melt-cast samples (A) crude-**1**-PhB and (B) fine-**1**-PhB under 365 nm UV light and after turning off the light source. (C) Room-temperature steady-state emission and delayed emission (1 ms delay) spectra of crude-**1**-PhB and fine-**1**-PhB. (D) Room-temperature phosphorescence decay of crude-**1**-PhB and fine-**1**-PhB.



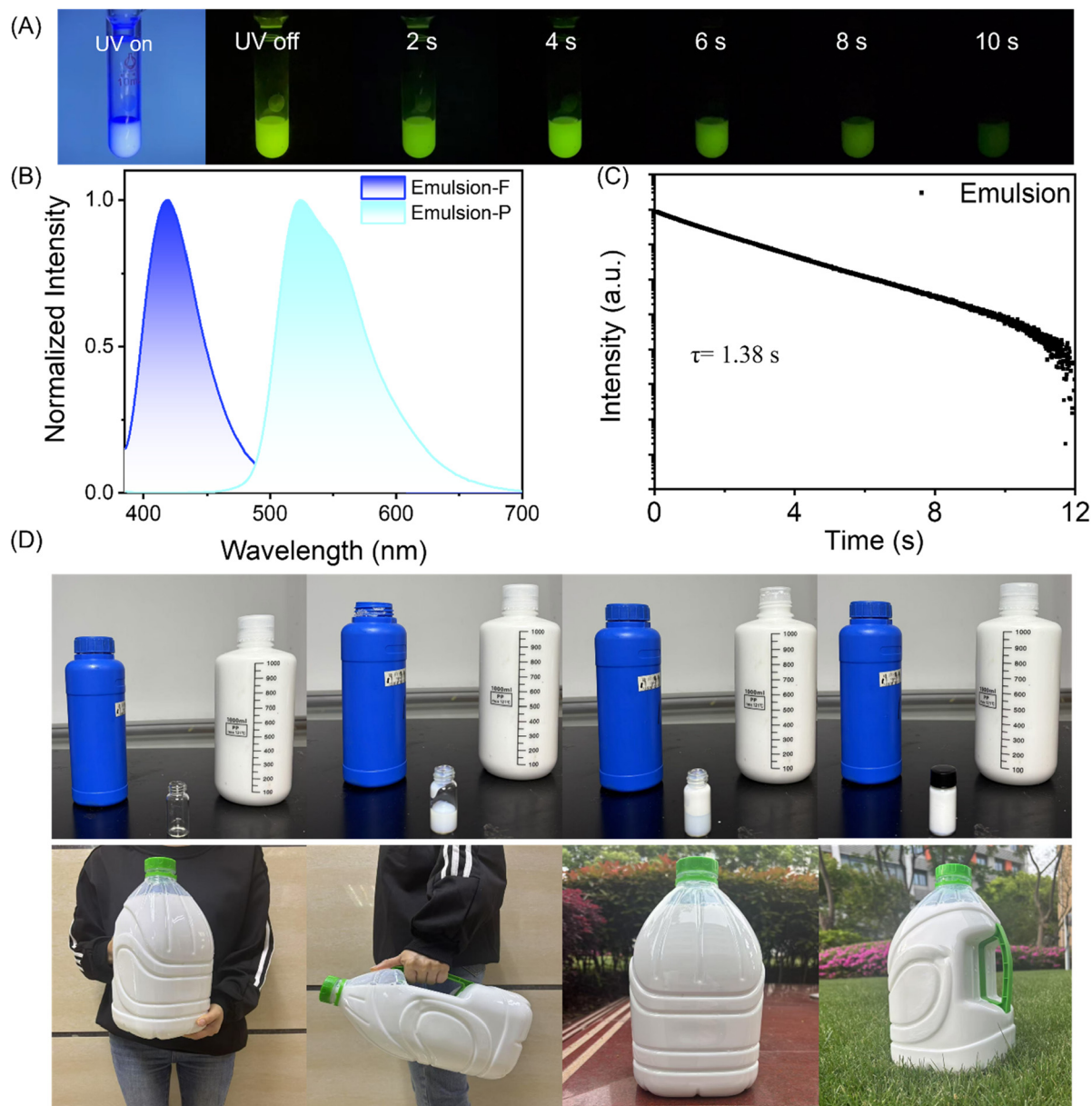


Fig. 3 (A) Photographs of the emulsion under 365 nm UV light and after ceasing the light source. (B) Room-temperature steady-state emission and delayed emission (1 ms delay) spectra of the emulsion. (C) Room-temperature phosphorescence decay of the emulsion. (D) Photograph of a binary blend afterglow coating and a barrel afterglow emulsion.

emulsion, and vinyl acetate emulsion, respectively (Fig. 3D). These afterglow coatings are safe and reliable, with a high solid content (Table S1) and no pungent odour during use after being applied to the surface of a Petri dish and dried, the afterglow coating applied to the glass sheet exhibits excellent photophysical properties in an oxygen atmosphere, with an afterglow duration of 6 to 12 s, and the afterglow duration of the coating applied to polyethylene terephthalate (PET), metal and cement sheets can still reach more than 5 s (Fig. 4 and Fig. S8–S13). The phosphorescence peaks were similar to those of the 1-PMMA emulsion (Table S2). This demonstrates the potential for creating stable and commercially feasible afterglow coatings with improved physical properties.

In addition, these afterglow coatings exhibit high solid content and a variety of excellent physical properties. All four coatings show good stability, maintaining their integrity over 48 hours, 168 hours, and beyond (Fig. S14). Due to the presence of silane monomers in blended polymer emulsions, coatings A, B, and C have water contact angles greater than 80° (Fig. S15–S18), exhibiting hydrophobicity and stain resistance. Stains on the smooth surface can be easily wiped off, revealing bright green phosphorescence (Fig. 5A, B and Fig. S19–S22).

Thermogravimetric analysis (TGA) results indicate that coatings A, B, and C have better thermal stability in a nitrogen atmosphere, with degradation beginning only at around 325°C (Fig. 5C). Furthermore, chemical resistance tests were conducted by fully



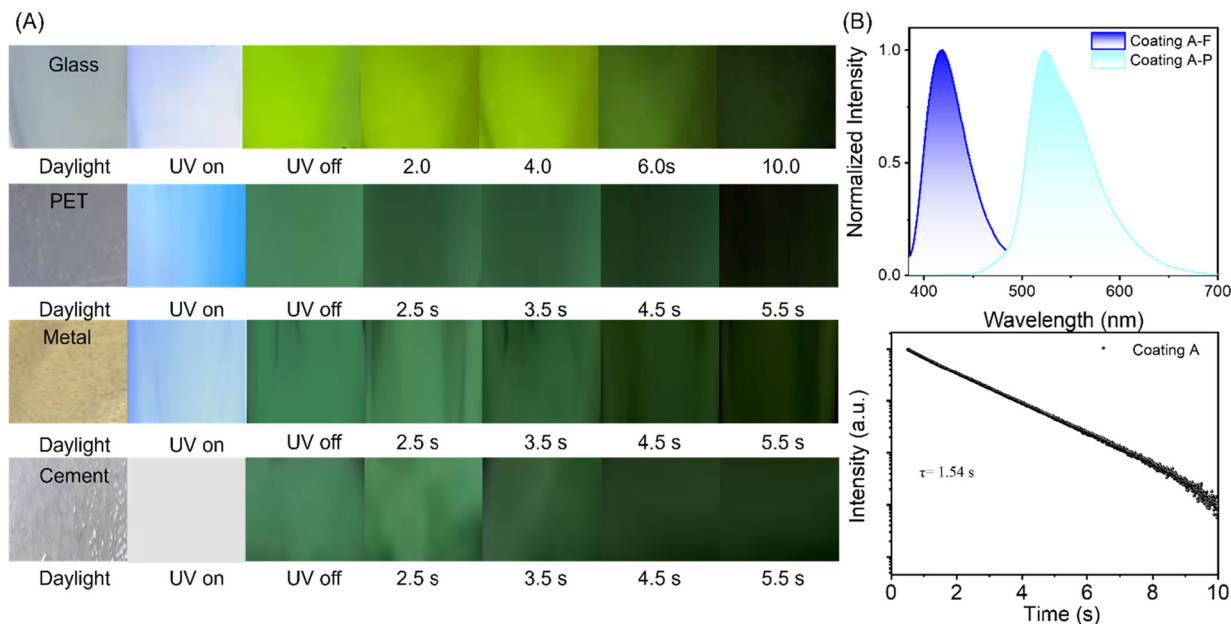


Fig. 4 (A) Photographs of coating A under 365 nm UV light and after ceasing the light source on different sheets. (B) Room-temperature steady-state and delayed emission (1 ms delay) spectra of coating A and room-temperature phosphorescence decay of coating A in a glass sheet.

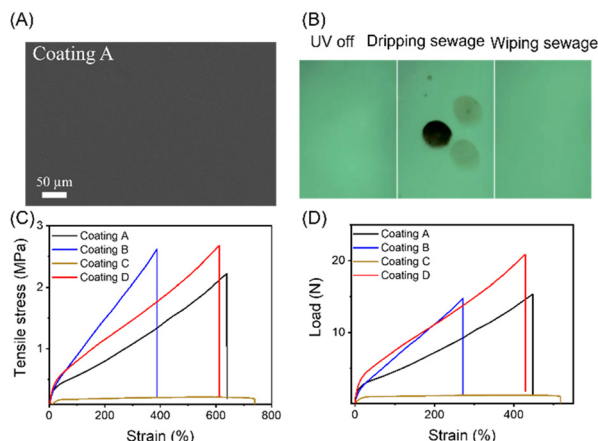


Fig. 5 (A) SEM image of coating A. (B) Photographs of cleaning up sewage by wiping and by wiping performed on the afterglow panels in the UV-off mode. (C) Tensile stress-strain, and (D) load-strain of coating A, coating B, coating C and coating D.

immersing the coatings in 2% H_2SO_4 solution, 1 M NaOH solution, and 3% high-concentration NaCl solution for 72 hours. The results show no bubbling or cracking on the surface of any of the four coatings, and their size remains unchanged, indicating a certain degree of chemical resistance (Fig. S23–S25). These findings highlight the excellent performance of these afterglow coatings in terms of stability, hydrophobicity, stain resistance, thermal stability, and chemical resistance, making them promising for practical applications. Besides this, the tensile properties of the four coatings were investigated. The tensile stress of coatings A, B, C, and D was 2.22 MPa, 2.62 MPa, 0.22 MPa, and 2.68 MPa, respectively, while the elongations at break were 639.5%, 388.1%, 739.5%, and 612.9%

(Fig. 5). These results demonstrate that the four coatings possess excellent tensile strength, ductility, and processability (Fig. 5 and 6). Additionally, even under deformation, they maintain their bright green afterglow. This is because the stretching, twisting, and bending of the coatings do not alter the rigid microenvironment of the compound 1 in PMMA, and non-radiative deactivation of the triplet state does not increase (Fig. 6C, D and Fig. S26–S28).

Therefore, the advanced technology of these afterglow coatings, along with their alignment with market demands, greatly expands the potential applications of these coatings and significantly increases their added value. Lastly, due to their ultra-high transparency and excellent mechanical properties, these coatings can be applied to substrates with printed patterns, offering additional protection to the substrate surface while preserving the original patterns. This makes the coatings resistant to scratches and stains during daily use, while simultaneously providing outstanding photophysical performance. The RTP performance of the samples in this study is stable under ambient conditions during storage. To investigate their durability, we treat them with harsh conditions. For example, by exposing the samples to strong UV exposure, high humidity and strong mechanical stress, we find that the afterglow behaviours are retained while the RTP performance decreases because of the harsh conditions (Fig. S29–S31). Besides, the water-based polymeric systems are friendly to the environment when compared to other coating materials such as acrylic emulsions, alkyds, or polyurethanes (Text S1).

Conclusions

In summary, we designed and synthesized a cost-effective fluorene-based luminescent molecule, compound 1. By using a two-component doping strategy and emulsion



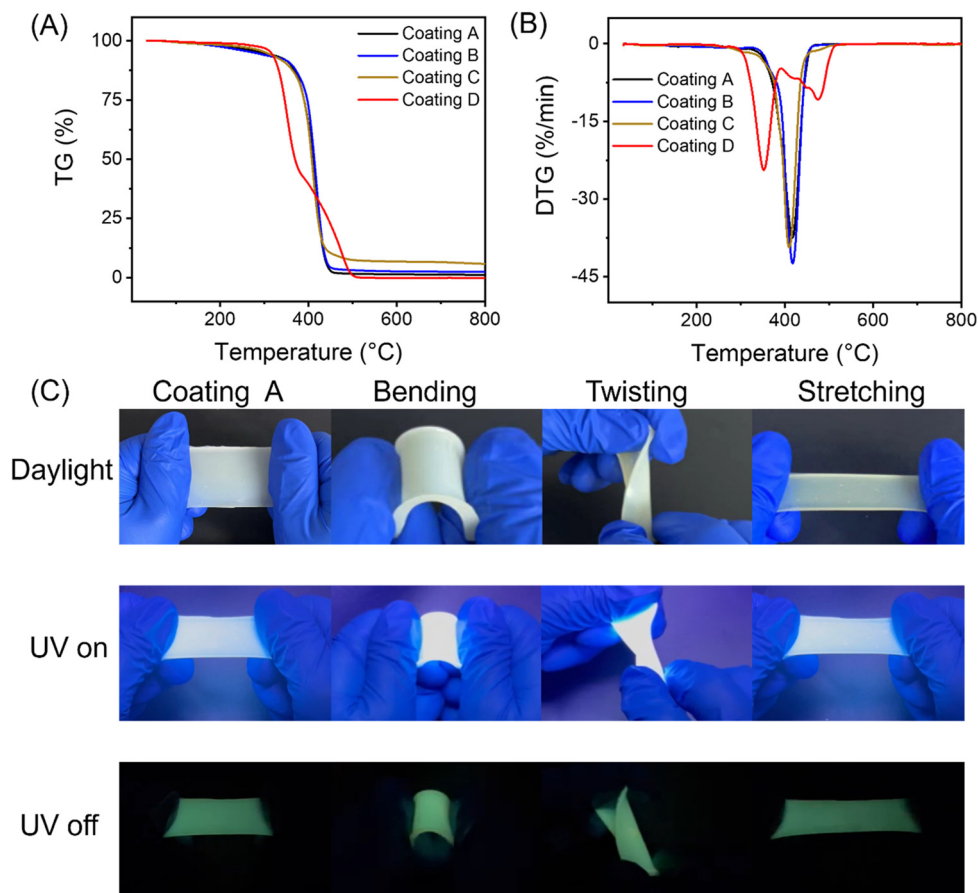


Fig. 6 (A) Thermogravimetric analysis, and (B) derivative of thermal gravity of coating A, coating B, coating C and coating D. (C) Photographs of coating A under twisting, bending and stretching conditions under daylight, 365 nm UV light and after ceasing the light source.

polymerization, we successfully prepared a long-afterglow luminescent emulsion suitable for large-scale production. This emulsion was then mixed with silane-acrylate emulsion, butyl acrylate emulsion, styrene-acrylate emulsion, and ethylene-vinyl acetate emulsion to produce four types of coatings. These coatings exhibit bright green phosphorescence with a maximum lifetime of up to 1.5 s. Additionally, the coatings possess multifunctional properties, including hydrophobicity, stain resistance, chemical resistance, and excellent thermal stability. Furthermore, the coatings demonstrate good mechanical properties and flexibility, allowing for easy processability while providing additional protection without compromising the underlying substrate patterns. This work provides robust technical support for the production of high-value-added coatings. Moreover, the integration of afterglow and coating technologies lays a solid foundation for the development of RTP materials.

Author contributions

Boyi Fu data curation, methodology, validation; Yuanyuan Chen data curation, methodology; Qianqian Yan writing; Tengyue Wang software; Xixi Piao writing; Kaka Zhang conceptualization, funding acquisition, supervision, writing – review & editing.

Conflicts of interest

The authors declare no competing financial interest.

Data availability

The authors confirm that the data supporting the findings of this study are available within the article and its supplementary information (SI). Supplementary information includes molecular synthesis, material fabrication, instrumentation details, as well as supporting figures of the photophysical and material properties. See DOI: <https://doi.org/10.1039/d5qm00333d>.

Acknowledgements

We acknowledge the financial support from the National Natural Science Foundation of China (22475228, 22175194), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB0610000), Hundred Talents Program from Shanghai Institute of Organic Chemistry (Y121078), Pioneer Hundred Talents Program of Chinese Academy of Sciences (E320021), and Ningbo Natural Science Foundation (2023J243).



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